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LETTER TO THE EDITOR

Anomalous superconducting response in $CeRu_2$ and $(Ce_{0.95}Nd_{0.05})Ru_2$: evidence of a first-order transition

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Abstract. Results of detailed magnetization studies are presented, which provide thermodynamic evidence of a first-order transition in the superconducting mixed state of $CeRu_2$ and $(Ce_{0.95}Nd_{0.05})Ru_2$.

Recently much attention has been focused on the superconducting (SC) mixed state of the C-15 Laves phase compound $CeRu_2$, which shows an anomalous magnetic response in its isothermal magnetization in the vicinity of the $H_{C2}(T)$ line for $T \leqslant 0.9T_C$ [1–10]. This anomalous response is quite robust in nature and is also observed in Nd-doped $CeRu_2$ samples [11, 12]. A similar anomalous response has also been observed recently in some other paramagnetic superconductors, i.e., UPd_2Al_3 [7, 13], $CeCo_2$ [14, 15], UPt_3 [16] and $Yb_3Rh_4Sn_{13}$ [17]. The anomalous isothermal response is accompanied by greatly enhanced irreversibility in the magnetization. This indicates that the critical current density J_C also has a peak as a function of field.

At the moment the most important question regarding this anomalous superconducting response is the following: is this response due to a dynamical change in pinning properties, i.e., the classical peak effect (CPE) [18], or due to a phase transition in the thermodynamic sense? In this letter we address this particular question, and show from a detailed study of the minor hysteresis loops in the anomalous regime that the observed behaviour cannot be correlated with CPE in any straightforward manner. We then present measurements of the equilibrium magnetization that establish the onset of the anomalous response as a first-order phase transition. We emphasize that the results to be discussed here are general properties of at least four samples of $CeRu_2$ and 5% Nd-doped $CeRu_2$, obtained from three different sources (Imperial College, London; University of Kentucky and Los Alamos National Laboratory). These samples, in general, are characterized using x-ray diffraction study and metallography. The sample from Los Alamos was subjected to more detailed characterization and has been used earlier in many measurements [19]. The Imperial College samples (one pure and one 5% Nd-doped $CeRu_2$) were also characterized for homogeneity with resistivity measurements. Magnetization was measured using a Quantum Design SQUID magnetometer (MPMS-5) and to minimize the field inhomogeneity and sample movement we used a single scan of 2 cm length in the 'fixed-range' mode. The maximum field inhomogeneity in a 2 cm scan in an applied field of 4 T is 2 Oe. We checked the regression value and SQUID profile regularly and, except for the small field interval of the dia- to paramagnetic crossover regime, the SQUID profile is always dipolar with a regression value of more than 0.9.

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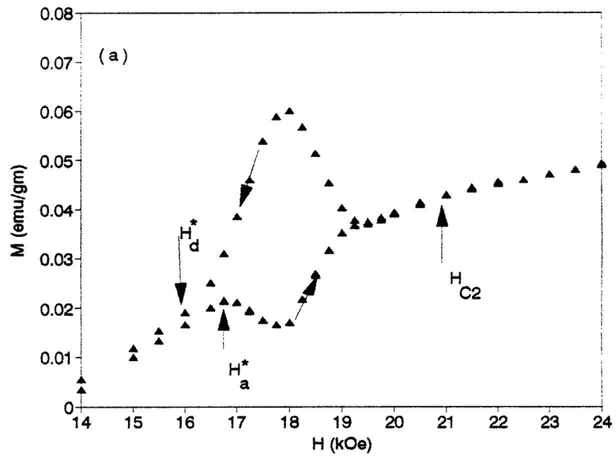
In figure 1 we show the anomalous magnetization behaviour for two polycrystalline samples of pure $CeRu_2$ (one obtained from Los Alamos National Laboratory (MD1) and the other from Imperial College (IC3)) and one polycrystalline sample of $(Ce_{0.95}Nd_{0.05})Ru_2$ at $T = 4.5$ K. The magnetization (M) field (H) (M–H) curves are obtained by raising the field from $-H_{C2}$ to 0 to H_{C2} (the ascending envelope curve) and by lowering the field from H_{C2} to 0 (the descending envelope curve). In the ascending field case, a large drop in magnetization starts at a field H_a^*. In the descending field case, the anomaly is completed at a field H_d^*, which is distinctly below H_a^*. This hysteresis in the field at which the anomaly appears (disappears) in the ascending (descending) cycle has also been observed in good single-crystal samples of $CeRu_2$ (see figure 2 of [10]) and taken as evidence that the transition which starts in the ascending field cycle at H_a^* is a first-order transition [6, 7, 10].

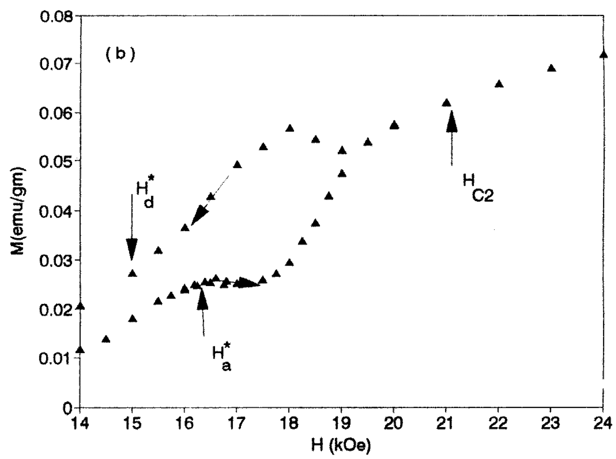
In figure 2(a) we present the minor hysteresis loops (MHLs) initiated at various H_is within the anomalous field regime (at 4.5 K), in the ascending field cycle for the pure $CeRu_2$ sample MD1. Here, for the sake of clarity, we show only the forward leg of the MHLs. The MHLs initiated from the ascending envelope curve at fields $H \geqslant 18.5$ kOe saturate by hitting the descending envelope curve. The estimated value of the field for full penetration (H_{II}) is $\approx$100 Oe in this H regime. At fields below ($H_i - H_{II}$), the hysteresis in magnetization will be referred to as the saturation ΔM_H and this depends on J_C and the sample size D. In the field regime $H < 18$ kOe, since ΔM_H reduces as H falls, and H_{II} at 18.5 kOe is $\approx$100 Oe, the value of H_{II} is expected to be smaller than 100 Oe. We have obtained MHLs in the ascending cycle at fields between 15 and 19 kOe by reducing the field by up to 200 Oe. (For the sake of clarity we show data only for initiating fields $H = 15.5$, 16, 16.75, 17, 17.25, 17.5, 17.75, 18, 18.25 and 18.5 kOe, although we also have data at intermediate fields.) The MHLs appeared to have saturated, but always failed to reach the upper envelope curve. It is to be noted that within the critical state models (CSMs), the magnetization in an MHL can only reach saturation by hitting the envelope curves and that happens when the excursion field is greater than H_{II} [20]. (MHLs generated at fields lower than 16 kOe merge with the envelope curve with the estimated H_{II} being $\approx$50 Oe). We have also checked that starting at $H = 17.5$ kOe and 18 kOe, we could reduce H to 16.5 kOe without meeting the envelope curve. The saturated value of ΔM_H at 16.5 kOe is smaller when the minor loop is initiated at 17.5 kOe than when the field reversal is initiated at 18 kOe. This is inconsistent with the CSM and we have the interesting problem of saturation ΔM_H being dependent on the starting field. This problem does not occur when the MHL is initiated from above 18.5 kOe.

Qualitatively similar behaviour of the MHLs has also been observed in the other $CeRu_2$ sample IC3 as well as the 5% Nd-doped $CeRu_2$ sample, in the anomalous SC regime (see figure 2(b) and (c)).

Our studies of MHLs thus establish that the CSM cannot be used in the anomalous (H, T) regime of $CeRu_2$ and 5% Nd-doped $CeRu_2$, and here one is not dealing with a conventional peak effect.

Within the CSM, the saturation ΔM_H depends on J_C and the (transverse) sample dimension D. If J_C is independent of field, then ΔM_H depends linearly on D. Our interesting problem of saturation ΔM_H being dependent on the starting field then translates into the size D (of the sample exhibiting enhanced pinning) being dependent on the field at which the MHL is initiated. We attribute the enhancement of irreversibility above H_a^* to the formation of a new phase with enhanced J_C. The saturation ΔM_H is then dictated by the size D of this new anomalous phase which has enhanced pinning. We now consider the picture that as the anomalous SC phase is formed on raising the field through H_a^*, we go through a first-order transition where nucleation of the phase is in domains and their size





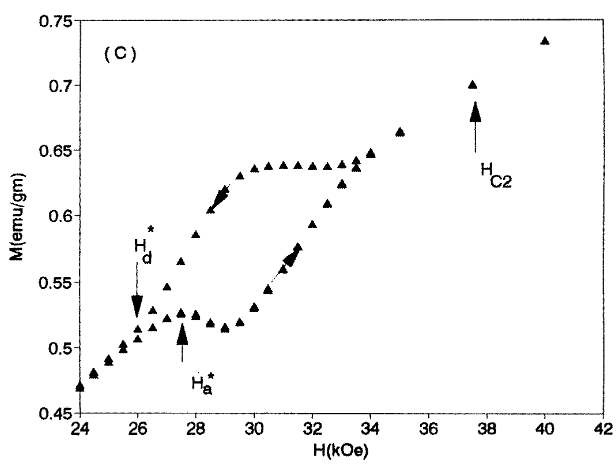


Figure 1. Enlarged magnetization (M) versus field (H) plot of $CeRu_2$ and $(Ce_{0.95}Nd_{0.05})Ru_2$ samples at 4.5 K, to highlight various characteristic features of the anomalous structure. (a) $CeRu_2$ sample MD1, (b) $CeRu_2$ sample IC3 and (c) $(Ce_{0.95}Nd_{0.05})Ru_2$ sample. As far as the difference in H_a^* and H_d^* is concerned, this figure is similar to figure 2 of [10].

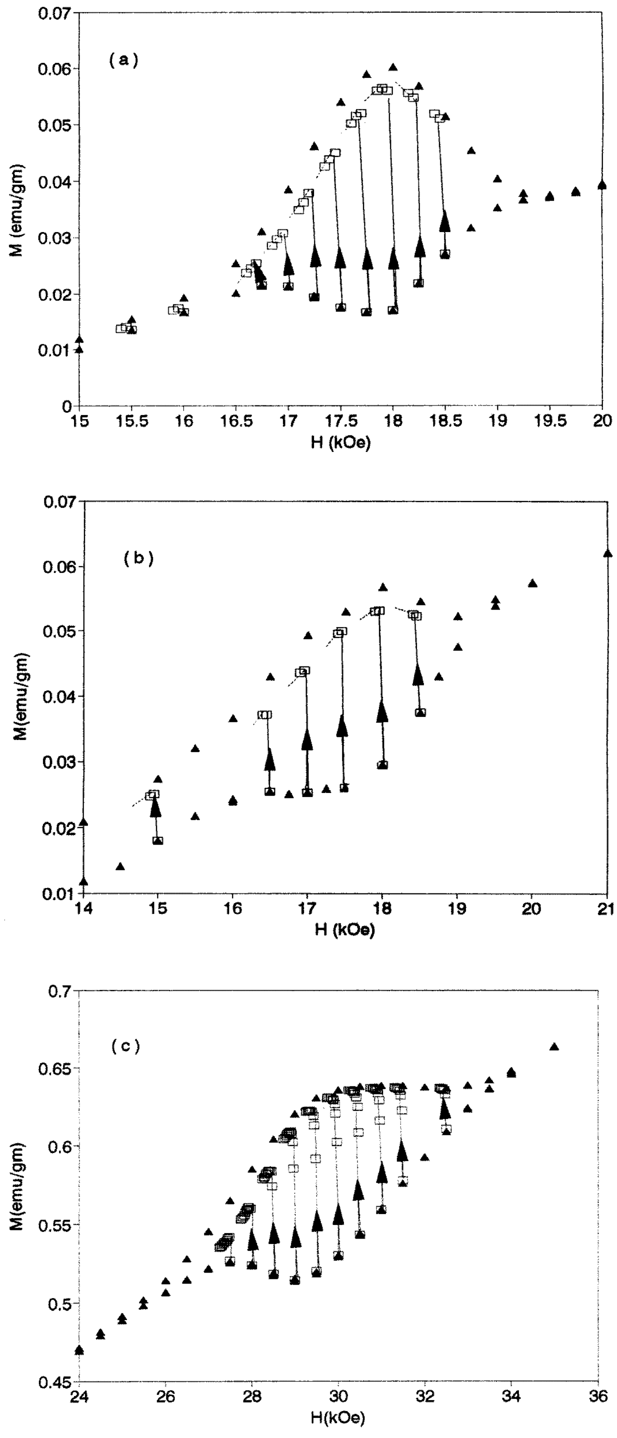


Figure 2. Forward legs of the minor hysteresis loops (MHLs), obtained in the anomalous regime for the $CeRu_2$ and $(Ce_{0.95}Nd_{0.05})Ru_2$ samples at $T = 4.5$ K. (a) $CeRu_2$ sample MD1, (b) $CeRu_2$ sample IC3 and (c) $(Ce_{0.95}Nd_{0.05})Ru_2$ sample. All these minor loops (□) are initiated in the ascending field cycle i.e. from the lower envelope curve. (▲) represent the envelope curve.

(or D) grows as we raise the field. This formation of domains and their growth takes place over the field range 16.5 kOe $\leqslant H \leqslant$ 18.5 kOe for the pure $CeRu_2$ samples (MD1 and IC3) and 27.5 kOe $\leqslant H \leqslant$ 31.5 kOe for the $(Ce_{0.95}Nd_{0.05})Ru_2$ sample. When we initiate an MHL at 17.5 kOe then we have domains of smaller D, but when we initiate an MHL at 18 kOe we have domains of larger D. Above 18.5 kOe (31.5 kOe) in the pure $CeRu_2$ samples (5% Nd-doped $CeRu_2$ sample), the anomalous phase is fully developed, and ΔM_H at say 18.75 kOe (31.75 kOe) does not depend on whether we only traverse up to 19 kOe (32 kOe) or all the way to $H > H_{C2}$.

The indications that the transition at H_a^* is first order have also been obtained from the hysteresis in ascending and descending field onsets in magnetostrictive [6, 7], magnetoelastic [21] and magnetoresistance [8] measurements.

All the measurements mentioned above gave strong but indirect indications of a first-order transition. We will now look for thermodynamic signatures of the isothermal transition at H_a^* being a first-order phase transition. There has recently been quite some discussion on the observation of first-order transitions of the vortex lattice [22]. The equilibrium magnetization M_{eq} is a thermodynamic quantity, whereas resistivity is not. A change in equilibrium magnetization, associated with vortex lattice melting in clean single crystals of HTSC, is directly observed in M against H scans because the magnetization is reversible in the neighbourhood of the transition [22]. In $CeRu_2$, on the other hand, the M against H is hysteretic in the neighbourhood of the transition. Extracting M_{eq} in such a case is non-trivial, and we shall present our prescription below. But first we shall bring out the importance of measuring M_{eq} near H_a^* as a 'failure test' of whether the transition at H_a^* is thermodynamically a first-order transition.

We first note that the field H_a^* at which the transition is seen rises as T falls. We note from the phase diagrams of $CeRu_2$ [6–8, 12] and 5% Nd-doped $CeRu_2$ [11, 12] that the high-field phase (above H_a^*) is also the high-temperature phase, and it thus has a higher entropy. Together with the Clausius–Clapeyron equation,

$$L = T\,\Delta S = -T\,\Delta M(\mathrm{d}H^*/\mathrm{d}T) \qquad (1)$$

we can assert that if the transition at H_a^* is a first-order transition, then M_{eq} must rise as H crosses H_a^*. A drop in M_{eq} would imply a failure of the first-order transition hypothesis, and the measurement of M_{eq} against H is thus an essential 'failure test'.

We now address the question of extracting $M_{eq}(H)$ from a hysteretic M against H. The CSM states that for large H, $M_{eq}(H)$ is the arithmetic mean of $M\uparrow(H)$ and $M\downarrow(H)$. Here both $M\uparrow(H)$ and $M\downarrow(H)$ correspond to saturation magnetizations, i.e. the sample has been fully penetrated by shielding currents flowing in a single sense [23]. As has been argued above, in the neighbourhood of H_a^* we have domains of a new phase, which supercool on reducing H and whose size remains fixed on the MHL. The MHL reaches a saturation value $M_{ML}\downarrow(H)$ when these domains are fully penetrated by unidirectional shielding currents. We obtain $M_{eq}(H)$ as the arithmetic mean of $M\uparrow(H)$ and $M_{ML}\downarrow(H)$. Note that we use $M_{ML}\downarrow(H)$ instead of the descending envelope curve value because the envelope curve corresponds to supercooled domains of larger size.

We show in figure 3 the $M_{eq}(H)$ at 4.5 K for the two pure $CeRu_2$ samples and $(Ce_{0.95}Nd_{0.05})Ru_2$, obtained using the MHLs. We note a pronounced rise as H crosses H_a^* and enters the anomalous regime. The fact that there is a rise in $M_{eq}(H)$ at H_a^* is consistent with what is expected from equation (1) for a first-order transition. In the pure $CeRu_2$ sample IC3 and the 5% Nd-doped $CeRu_2$ sample, which show a higher slope of background paramagnetic contribution (in comparison to the $CeRu_2$ sample MD1; see figure 1), the rise in M_{eq} at the onset of the anomalous regime is relatively subtle.

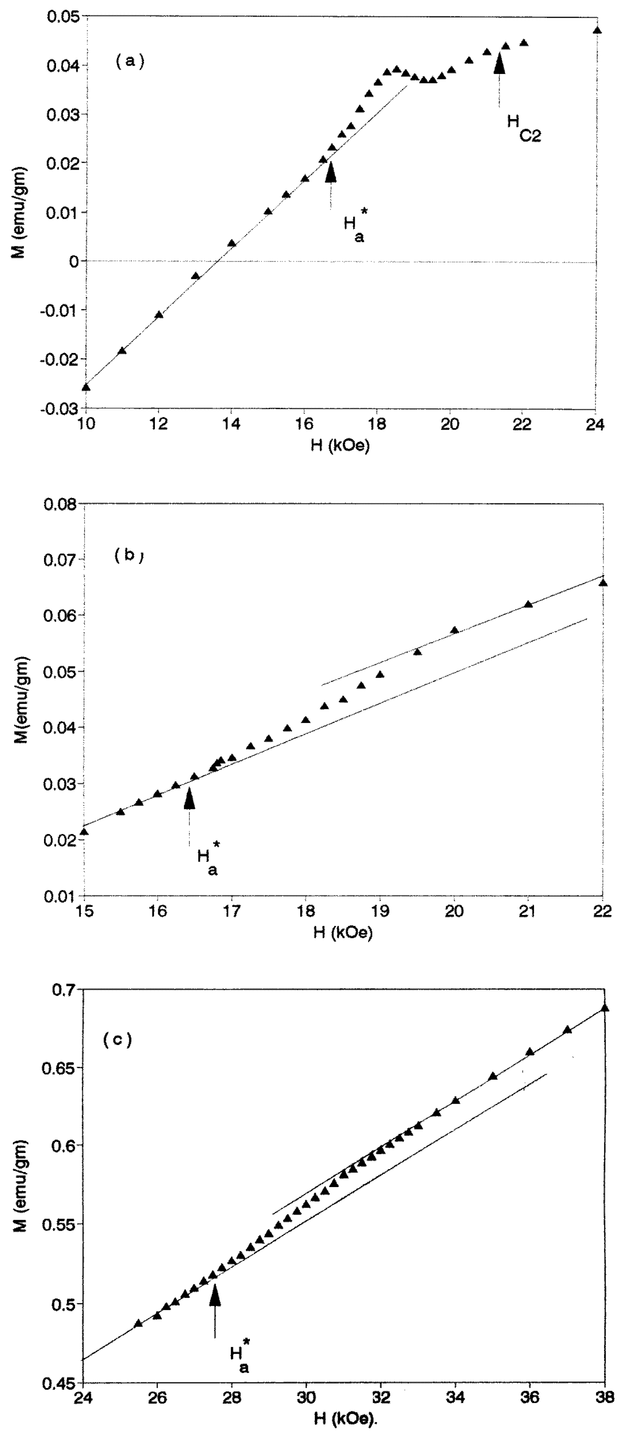


Figure 3. Equilibrium magnetization (M_{eq}) versus field (H) plot at $T = 4.5$ K for (a) $CeRu_2$ sample MD1, (b) $CeRu_2$ sample IC3 and (c) $(Ce_{0.95}Nd_{0.05})Ru_2$ sample. The straight line is drawn to highlight the small but distinct rise in magnetization at H_a^*.

In the pure $CeRu_2$ sample MD1, there exists a distinct minimum just below H_{C2} in the M_{eq} against H plot at $T = 4.5$ K which becomes quite diffused with the increase in T. This minimum, however, is not visible (at least down to 3.5 K) in the pure $CeRu_2$ sample IC3 as well as the 5% Nd-doped $CeRu_2$ sample (see figure 3(b) and (c)). It should be noted here that in the last two samples the background paramagnetic contribution is perceptibly higher. A subtle minimum has also been observed earlier, between the anomalous magnetization bubble and H_{C2}, in other samples (both polycrystalline and single crystal) of $CeRu_2$ [2, 7] and its origin remains unexplained. A similar behaviour has also been reported in the superconducting compound $CeCo_2$ [14]. A tentative explanation for such a minimum in terms of partial Kondo compensation of Ce magnetic moments has been provided by Coles [1, 4, 14].

We provide an estimate of the latent heat for the sample MD1 using equation (1). We use for $H_a^*(T)$ the field values at which the anomaly in M against H is first seen during the ascending field case, and this yields $(\mathrm{d}H_a^*/\mathrm{d}T) = -1.3 \times 10^4$ Oe K^{-1} at 4.5 K. Using ΔM_{eq} from figure 3(a), we obtain a latent heat of 40 μJ g^{-1} at $T = 4.5$ K. Given the uncertainties in determining ΔM_{eq} and $\mathrm{d}H_a^*/\mathrm{d}T$, this estimate of latent heat should be accurate to within 10%.

Summarizing the results presented above, in the SC mixed state of $CeRu_2$ there exists enough evidence of a distinct first-order transition from an Abrikosov flux lattice (AFL) state to a new SC state with enhanced pinning. The picture of a Fulde–Ferrel–Larkin–Ovchinnikov (FFLO) state [24] and its extension GFFLO state [25], which predicts the existence of a partially depaired and spatially inhomogeneous superconducting state in the high-field regime near H_{C2}, seem to be in a good position to explain many of the results described above. While a rise in equilibrium magnetization is required by the macroscopic Clausius–Clapeyron relation, Gruenberg and Gunther [26] predicted theoretically a rise in the equilibrium magnetization as a result of a first-order transition from an AFL state to the FFLO state. Within the FFLO state the enhanced magnetization irreversibility can be attributed to the staggered order parameter of the FFLO state causing segmentation of the flux lines which in turn can be pinned relatively easily [7]. For the confirmation of the existence of a first-order transition, one now needs a careful calorimetric study of the latent heat.

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